Towards a Complete Electronic Database of PAHs and the Identification of Resolved DIBs

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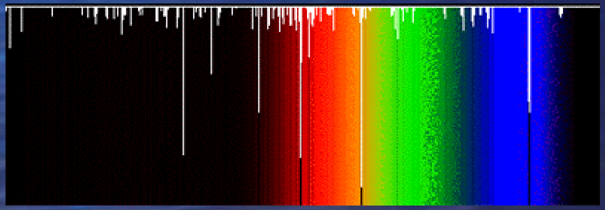
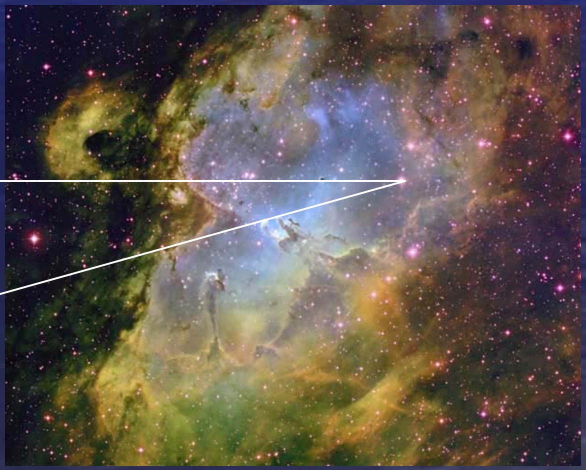
The Diffuse Interstellar Bands (DIBs)

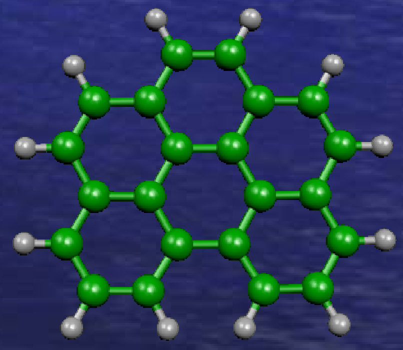
- Interstellar absorption bands first discovered by Heger in 1921. More than 300 diffuse bands in the visible and near infrared.
- No carriers have ever been identified!
- Providing crucial information on the chemical compositions of galaxies and interstellar medium, on the energy balance, chemical evolution of the universe and origin of life…





The PAH–DIB Hypothesis

- PAHs (neutral or ionic) may be responsible for some of the DIBs.
- Abundance of elements in the universe: H, He, O, C, N, Ne…
- PAHs are remarkably photo stable.
- PAHs have been identified in meteorites.
- PAHs and the infrared emission bands.



We Are Lottery Players

- Scientists are lottery players who are hoping to hit the Jack Pot by chance.
- Unfortunately, up to date only very limited PAHs have been studied either experimentally or theoretically: ~ 0.1% PAHs containing up to 10 fused benzene rings.
- A big question to ask therefore is: "exactly how many PAHs are out there and what PAHs should we study?"

Computer Enumeration of PAHs

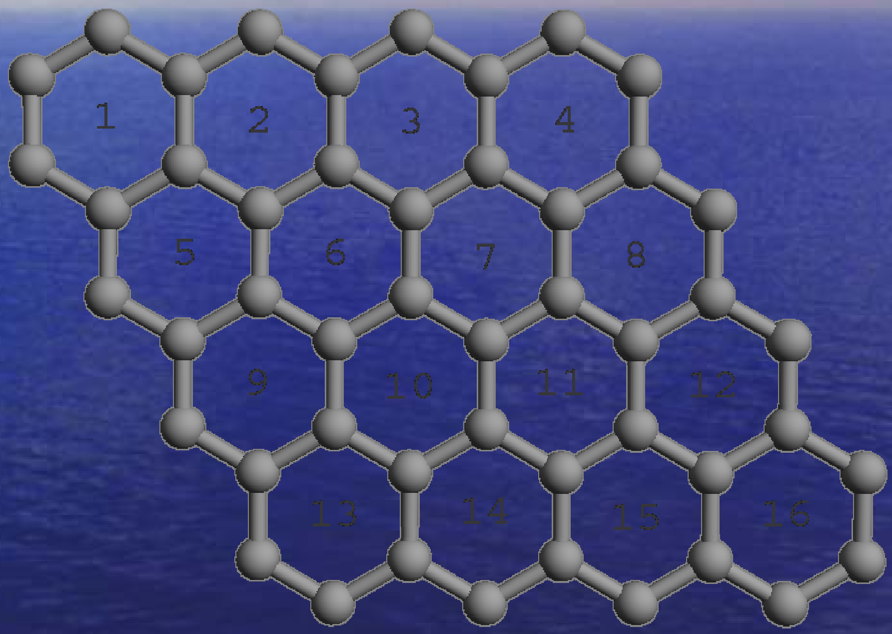
- The ideal carbon skeleton of a PAH is a "polyhex" that consists of *h* fused benzene rings.
- By "ideal", we mean all benzene rings in the polyhex are identical regular hexagons.
- How many polyhexes exist for a given number of *h* hexagons? Harary offered $100 for the solution to this difficult problem in 1968.

A Working Algorithm

- Cell growth: polyhexes with h hexagons are generated from polyhexes with $h - 1$ hexagons.
- Each time a new polyhex is generated, we transform it using each of the 12 symmetry operations.
- Each transformed polyhex is then converted into its SIR and compared to existing SIRs – the most time consuming step.
- A balanced search tree is used to store the SIRs.

The Honeycomb Grid

- All polyhexes with h hexagons can be contained in a $h \times h$ block honeycomb grid.
- Each hexagon, or "cell", is represented by one grid point located in its center of mass.



A 4×4 honeycomb grid.

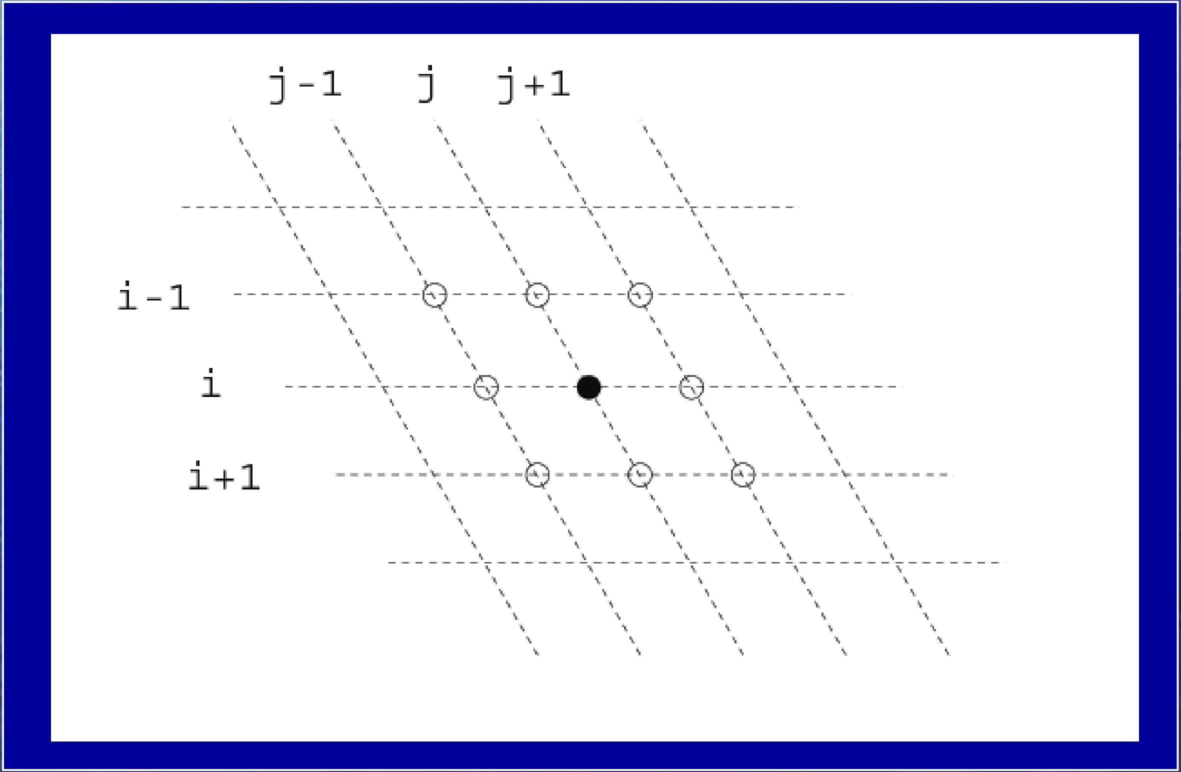
The Index Representation

- A polyhex can be represented by the cell numbers of its constitution cells, denoted as C(i, j, …), where i, j, … are the cell numbers.
- Index Representation: the cells of the T-shape are represented by their indices.
- Standard Index Representation (SIR).

$$C(1,5,2,6) \equiv \begin{pmatrix} 1 & 2 & 1 & 2 \\ 1 & 1 & 2 & 2 \end{pmatrix} \equiv \begin{pmatrix} 1 & 1 & 2 & 2 \\ 1 & 2 & 1 & 2 \end{pmatrix}$$

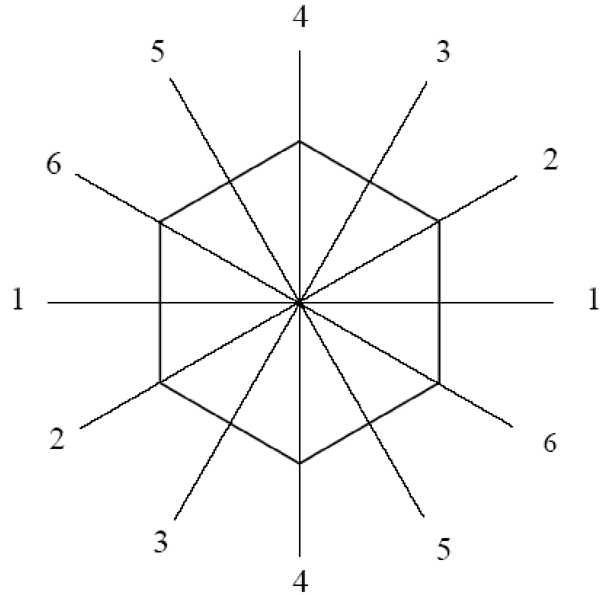
Cell Connectivity

- Each cell (grid point) is connected with six cells (grid points):



Symmetry Operations

- One translation.
- Six rotations: E, C_6, C_{-6}, C_3, C_{-3}, C_2.
- Six reflections:



The six mirrors of the honeycomb grid: $1-\sigma_x$, $2-\sigma''_y$, $3-\sigma'_x$, $4-\sigma_y$, $5-\sigma''_x$, $6-\sigma'_y$.

Transformation Matrices

$$M(E)=\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix},\quad M(C_6)=\begin{pmatrix}0 & -1\\ 1 & 1\end{pmatrix},\quad M(C_{-6})=\begin{pmatrix}1 & 1\\ -1 & 0\end{pmatrix},$$

$$M(C_3)=\begin{pmatrix}-1 & -1\\ 1 & 0\end{pmatrix},\quad M(C_{-3})=\begin{pmatrix}0 & 1\\ -1 & -1\end{pmatrix},\quad M(C_2)=\begin{pmatrix}-1 & 0\\ 0 & -1\end{pmatrix},$$

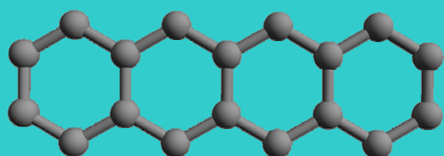
$$M(\sigma_x)=\begin{pmatrix}-1 & 0\\ 1 & 1\end{pmatrix},\quad M(\sigma_x')=\begin{pmatrix}0 & -1\\ -1 & 0\end{pmatrix},\quad M(\sigma_x'')=\begin{pmatrix}1 & 1\\ 0 & -1\end{pmatrix},$$

$$M(\sigma_y)=\begin{pmatrix}1 & 0\\ -1 & -1\end{pmatrix},\quad M(\sigma_y'')=\begin{pmatrix}-1 & -1\\ 0 & 1\end{pmatrix},\quad M(\sigma_y')=\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}.$$

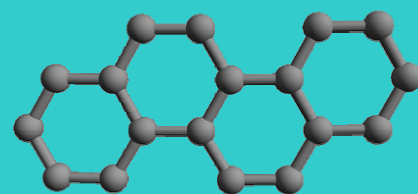
Number of Polyhexes & Cost

h	# PHs	Time (s)	*h*	# PHs	Time (s)
1	1	< 1	7	333	1
2	1	< 1	8	1448	6
3	3	< 1	9	6572	29
4	7	< 1	10	30490	167
5	22	< 1	11	143552	746
6	82	< 1	12	683101	6527

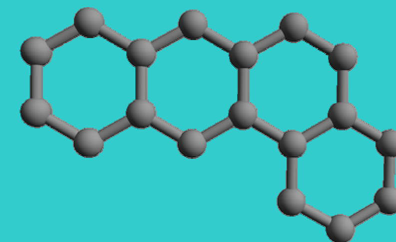
Polyhexes with h = 4



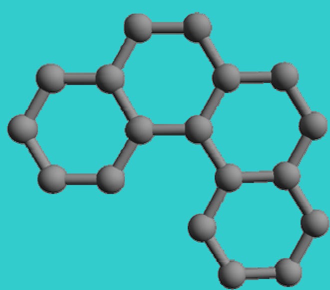
C(1,2,3,4)



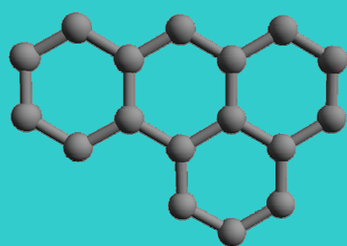
C(3,4,5,6)



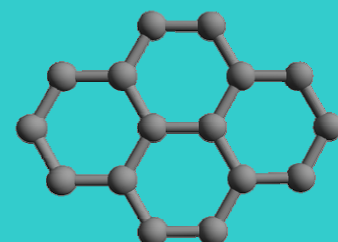
C(1,2,3,7)



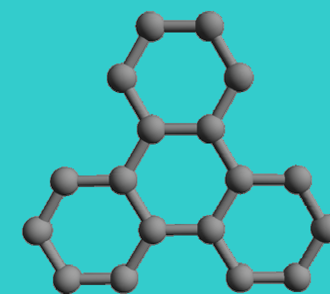
C(2,3,5,7)



C(1,2,3,6)



C(2,3,5,6)



C(2,6,7,9)

Geometries & Electronic Transitions

- "Model geometry" – H-C-C angles: $2\pi/3$; C-C bond: 1.397 Å; C-H bond: 1.084 Å.
- For geometry optimization, the Austin Model 1 (AM1) Hamiltonian is used.
- For electronic excitation energies, the Zerner's Intermediate Neglect of Diatomic Differential Overlap (ZINDO) method is used.
- The transition energies calculated at the model geometries are found to be better than those calculated at the geometries optimized at the AM1 level of theory.

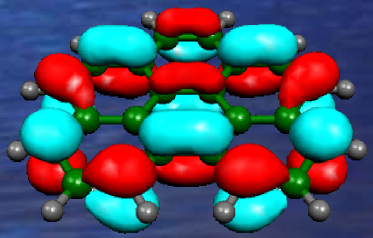
Calibration of the Database

- The current database contains all PAHs up to h = 10 (~ 40,000 PAH molecules).
- Sample space: 10 closed-shell neutral PAHs (18 rotational constants and 15 transition energies).
- Rotational constants: maximum relative error is 0.76% and the standard deviation is 0.39%.
- Electronic transitions energies: the mean is -1059 cm^{-1} (-0.13 eV); the largest deviation is -2757 cm^{-1} (-0.34 eV); standard deviation is 1322 cm^{-1} (0.16 eV).

Where the Database Was Built

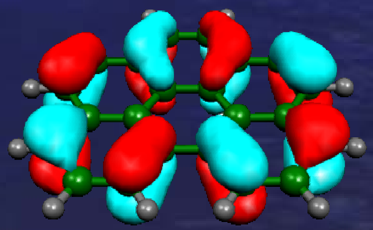
Electronic Properties of PAHs

- The rings are in the same plane in the electronic ground state (Cs).
- Conjugated π (A”) systems.
- Dominated by the $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$ transitions.
- Close shell: electronic transitions are in the UV and move to longer wavelength as the size grows.
- Open shell: electronic transitions are in the visible and near IR.



LUMO

Benzoperylene

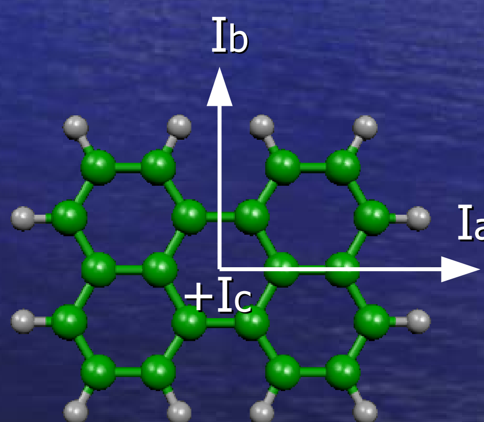


HOMO

Molecular Symmetry

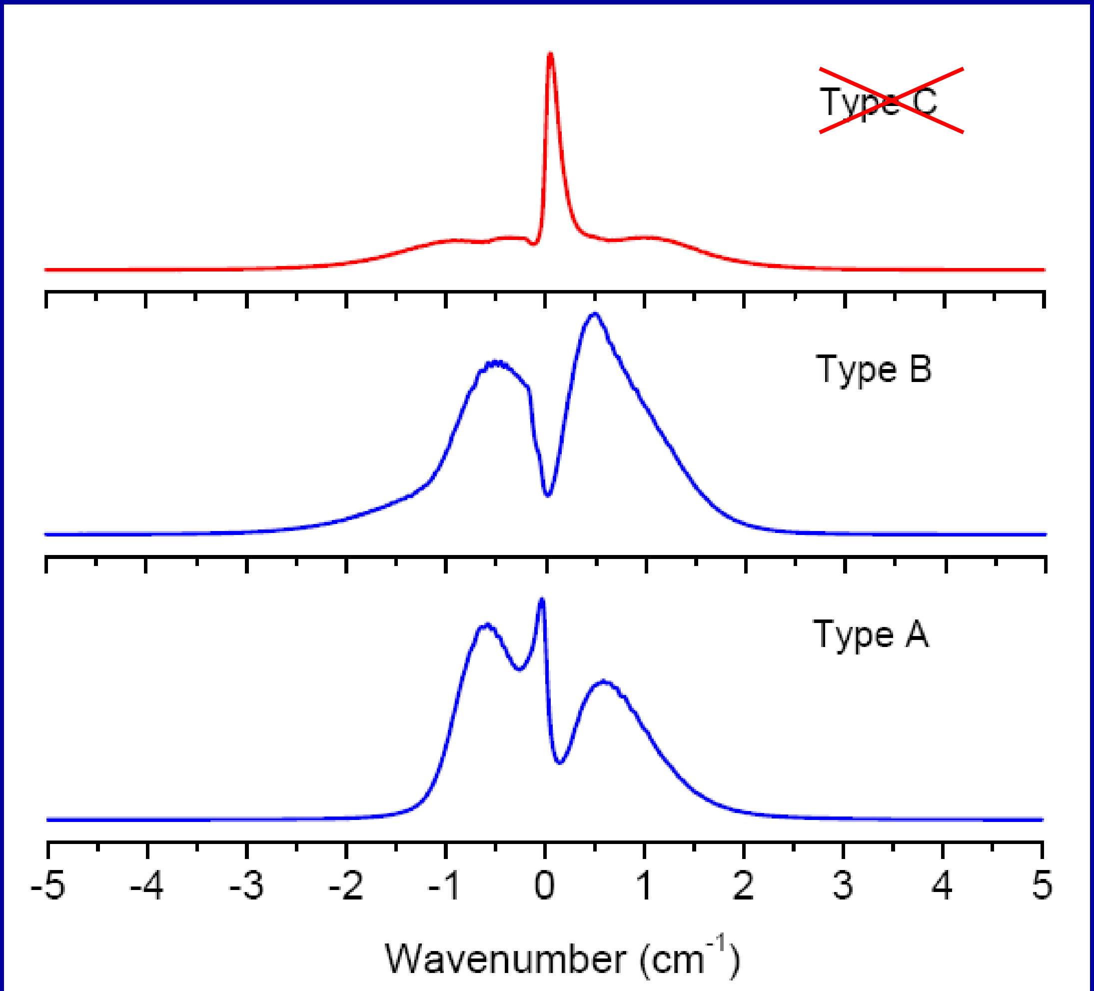
- In general, PAHs are asymmetric tops. I_c is perpendicular to the molecular plane and I_a and I_b lie in the molecular plane.
- Two independent rotational constants since $I_c = I_a + I_b$.
- If there exists a C_3 axis, the molecule is a oblate.
- Type-A and type-B band profiles.

Inertia Ellipsoid



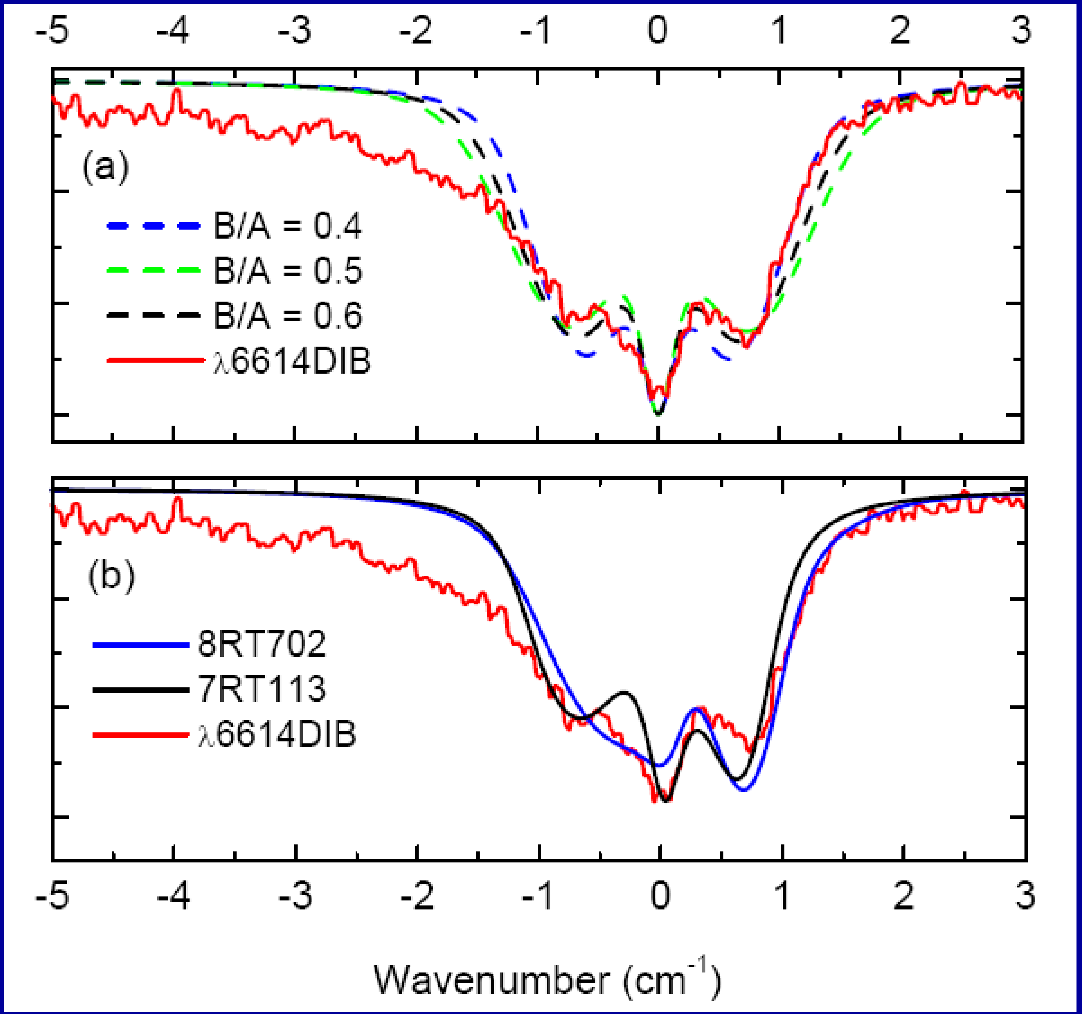
Principal Axes of Perylene

Band Profiles – Planar PAHs



Simulated vibronic band profiles using the rotational constants of the S_0 and S_1 electronic states of perylene [Tan & Salama, J.C.P. 122, 084318, (2005)]. The spectra are convoluted with a Lorentizan function with $\gamma = 0.05\ cm^{-1}$. $T_{rot} = 20$ K.

Deciphering The λ6614 DIB

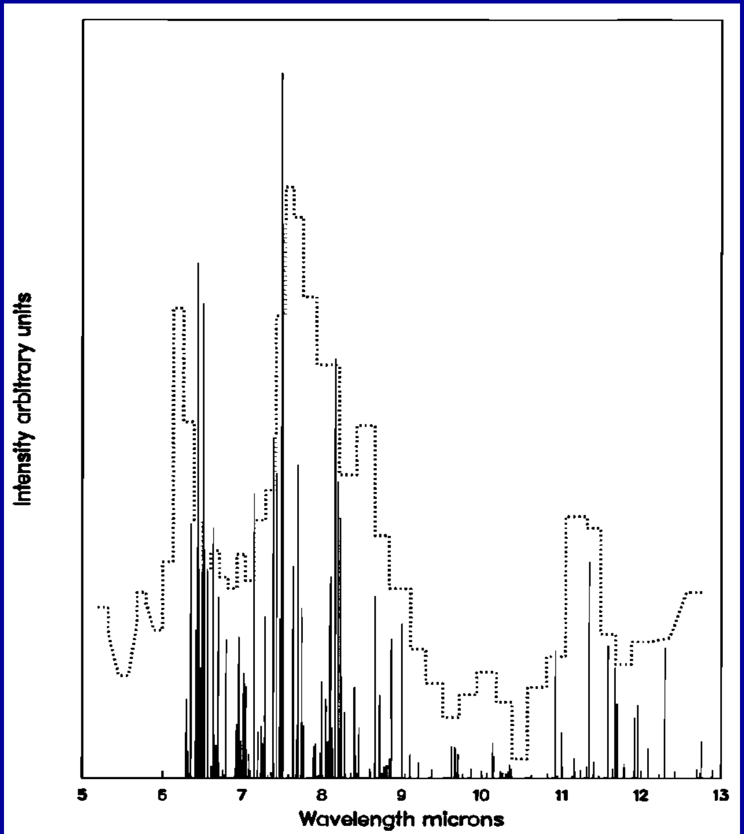


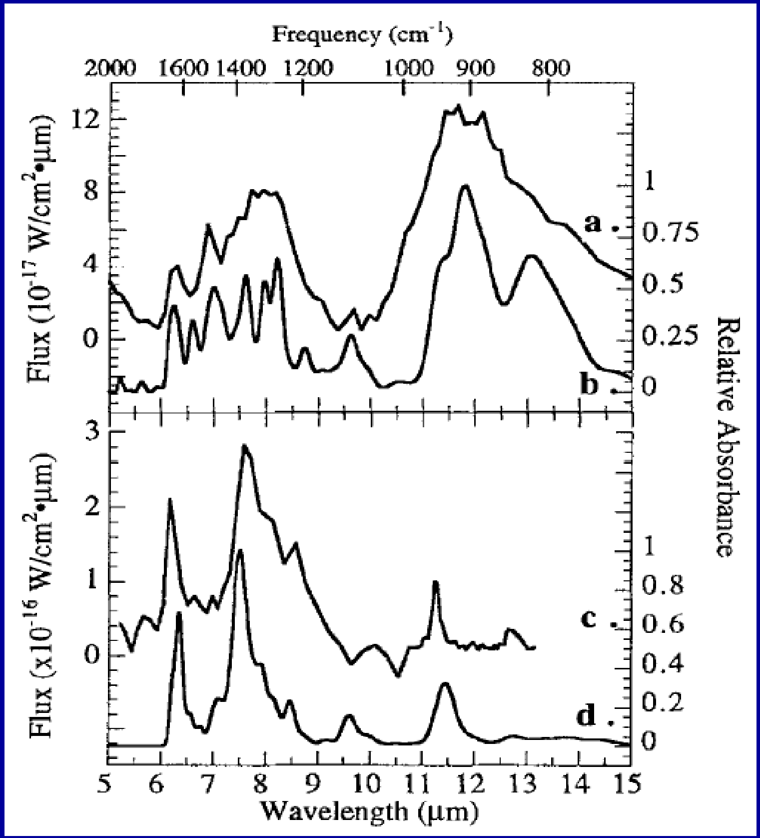
(a) Comparison of the λ6614 DIB (HD149757, Galazutdinov et al 2002) and simulated type-A profiles of planar PAHs, Trot = 54 K, A″ = 0.01 cm^{-1}, γ = 0.4 cm^{-1}. In the three simulations, A' = A″ = A, B' = B″ = B. B/A ratios are shown on the figure. (b). Comparison of the λ6614 DIB and simulated (TDDFT) profiles of 7RT113 and 8RT702.

Conclusions

- It is possible to build a “complete” electronic database of PAHs.
- Survey of all possible PAHs in this database is a very promising method to solve the PAH-DIB problem.
- For the first time, two closed-shell PAH cations are found to meet all constraints put on the λ6614DIB (wavelength, intensity, band profile, and ionization potential).

The Infrared Emission Bands





Dotted: IR spectrum of the Orion Nebula. Solid: theoretical spectrum of eight PAH cations. Langhoff, J. Phys. Chem., 100, 2819 (1996).

(a) & (c): Spectra of IRAS 22272+5435 & the Orion Nebula. (b) & (d) Spectra of mixed neutral and ionized PAHs. Allamandola et al, Ap.J. 511, L115 (1999).